Desorption of Dissolved Carbon Dioxide From Water Using Converging Nozzle : Effect of Temperature

By

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14212

Dissertation submitted in partial fulfilment of the requirements for the Bachelor of Engineering (Hons)

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the originality work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHAMAD ISKANDAR BIN CHE AYOB

ABSTRACT

The demands on natural gas keep increasing for the last several years. However, most of the world's reserves natural gas contain high amount of carbon dioxide. It is crucial to change current desorption technique with new compact size separator that can remove carbon dioxide instantly and feasible to be used at offshore platform. This project aims to investigate effect of temperature towards desorption of carbon dioxide from the solvent by using converging nozzle and how effectiveness of physical desorption of carbon dioxide change with temperature. This research covered concept of gas-liquid desorption, solubility of carbon dioxide, vapour liquid equilibrium, supersaturated ratio, effect of temperature towards desorption and effectiveness of the converging nozzle used. Laboratory work is done using special test rig. To convey effect of temperature, test was run at different temperature will other parameters kept constant (pressure, CO_2 loading). The amount of carbon dioxide in water after desorption was recorded and the trend of desorption was analysed. Effectiveness was determined by comparing mole fraction of carbon dioxide after desorption with at equilibrium condition (1bar). Result from experiment showed that desorption of carbon dioxide increase as temperature increase. Same goes to the effectiveness of converging nozzle which can go up to 78% at high temperature tested. The trend of desorption of carbon dioxide from water effect by trend of solubility of carbon dioxide in water system. From the research, it can be concluded that physical desorption of carbon dioxide from water by using converging nozzle always be more effective at high temperature.

ACKNOWLEDGEMENTS

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ABBREVIATIONS AND NOMENCLATURES

List of Abbreviations :

AGRU	Acid Gas Removal Unit
CNT	Classical Nucleation Theory
EOS	Equation of State
EUR	Estimated Ultimate Recovery
FYP	Final Year Project
IEA	International Energy Agency
LNG	Liquefied Natural Gas
MEA	Mono-ethanolamine
OGJ	Oil and Gas Journal
PSA	Pressure Swing Adsorption
PZ	Piperazine
RK	Redlich - Kwong
TCF	Trillion Cubic Feet
VLE	Vapour Liquid Equilibrium

List of Nomenclatures :

$C^*_{H_2CO_3}$	concentration of dissolved CO_2 and H_2CO_3 in equilibrium
E_A	activation energy
$H_{CO_{2,0}}$	Henry's coefficient of CO_2 in pure water
H_i	Henry's Constant
k	rate constant for desorption process surface
N	concentration of absorbed species
N_{nucl}	nucleation rate
Pb	high pressure
P_{CO_2}	partial pressure of carbon dioxide
P0	low pressure
T	temperature
x	kinetic order of desorption
x_i	mole fraction of component *i* in liquid phase
y_i	mole fraction of component *i* in gas phase

CHAPTER 1

INTRODUCTION

1.1 Background

For the last 40 years, global consumption of natural gas keep increasing. International Energy Agency (2013) stated that consumption of natural gas at the year 1965 are 23 trillion cubic feet (TCF) and this consumption keep increasing till reached 113 TCF in the year 2013 with forecast growth rate of 1.5% per year. In the year 2030, consumption of natural gas expected to reach up to 150 TCF (Huo,2012). This facts showed that world energy balance is tilting towards natural gas.

Natural gas can generally be divided into two which are sweet and sour natural gas. International Energy Agency (IEA) also reported that 43% of natural gas reserves in this world are sour natural gas. In South Asia, some of the natural gas reserves such as in Erawan and Platong fields in Thailand has carbon dioxide contents as high as 90% (Herzoq,2008). For the Malaysia, it is stated that by IEA(2010), the natural gas fields reserves contain carbon dioxide varies from 28% up to 87%.

Sour natural gas basically contain high amount of acidic gases including carbon dioxide (CO_2) and hydrogen sulphide (H_2S) High amount of CO_2, with the presence of water can corrode the pipelines. It is stated that by Hubbard (2010), the amount of CO_2 transmitted through pipelines into the end users must be less than 3%. Because of that, natural gas need to undergo pre-treatment in order to remove the CO_2.

Conventionally, pre-treatment of natural gas involve absorption and desorption column. Absorption column remove CO_2 from natural gas while desorption column regenerated the absorbent liquid to be used again. While many researchers focused on absorption of CO_2, desorption part is lack of study. Cost to operate desorption column is considered high and desorption column is big in size, thus consume large space and not

feasible to be used at offshore. The study on physical desorption process of CO_2 also very limited as most of the study focussing on absorption properties.

1.2 Problem Statement

With around half of natural gas reserved in the world is sour gas which contain significance amounts of CO_2, pre-treatment of the natural gas to remove this acidic gas need to be done. This pre-treatment section basically involves absorption and desorption parts. While most of the researchers focussed on removing CO_2 from natural gas, study must also be done on desorption part which remove CO_2 from liquid absorbent in order to regenerate or used it again.

Current technology for desorption of CO_2 is by using desorption column which is big in size and required large space. It is not convenient to be used at offshore platform. Alternative to change the desorption column to compact size separator which can remove CO_2 instantaneously through physical desorption process is crucial so that it can be applied at offshore platform. Before changing new way of desorption part, concept of desorption of CO_2 need to be understand first. The published journals and research regarding this area is very limited compare to absorption. Here come the motivation to do this research which focussing on physical desorption of CO_2 using converging nozzle with temperature as manipulated parameter.

1.3 Objectives

Objectives of this research project are:

i. To measure effectiveness of desorption of dissolved CO_2 from water at different temperature using converging nozzle.
ii. To investigate the effect of temperature towards the desorption of dissolved CO_2 in water at constant pressure.

1.4 Scopes of Studies

Several scopes of study covers throughout this research project. This research involve conducting of experiment in the lab by using special test rig that can desorb CO_2

instantly. Prior to that, concept of gas-liquid desorption and theory of physical desorption are studied. Limiting factors that govern gas-liquid desorption are determined. Through the lab work, effect of temperature towards desorption of dissolved CO_2 in water clearly be showed. Research also cover the comparison of desorption with the vapour liquid equilibrium condition at 1 bar to determine effectiveness of converging nozzle itself at different temperature of solvent.

Boundary of this research will be on effect of temperature towards desorption. Other parameters will be fixed so that effect of temperature can clearly be convey. The findings are recorded, critically analysed and be documented.

1.5 Relevancy and Feasibility of Project

This project is relevant with current situation in which sweet natural gas are depleting and most of the reserved natural gas is sour. As stated, it is very crucial to replace desorption column with compact size separator so that it can be used at offshore platform. Current desorption column is big in size, thus not feasible to be used at offshore. Physical desorption technique that can remove CO_2 instantaneously need to be applied, thus give impact towards current technology of regenerating or desorption part of pre-treatment section of natural gas. By changing to compact size separator, the technology of pre-treatment of natural gas will move to another step.

Throughout this project, the effect of temperature towards desorption of carbon dioxide from water through physical mean will be convey. This give significance as research on desorption is very limited and most authors only interest in exploring absorption of carbon dioxide. In macroscopic view, by conveying properties of desorption of CO_2 from solvent, this project will contribute to the development of the new physical desorption technique for the treatment of natural gas.

CHAPTER 2

LITERATURE REVIEW

This chapter includes literature review on the natural gas composition, conventional ways for pre-treatment of natural gas, concept of desorption as well as theory of solubility of gas (CO_2) in liquid and related theory behind the desorption process.

2.1 Production and Composition of Natural Gas

Natural gas is one of the important of world energy supply. It is considered as cleanest and safest source of energy (Crook, 2013). According to Crook (2013), ExxonMobil had predicted that in the next decade, natural gas will become most important global energy source due to the environmental benefits. Figure 2-1 below shows the world's production of natural gas from year 1980 up to year 2010 as per report by BP's 2012 Statistical Review of World Energy Data.

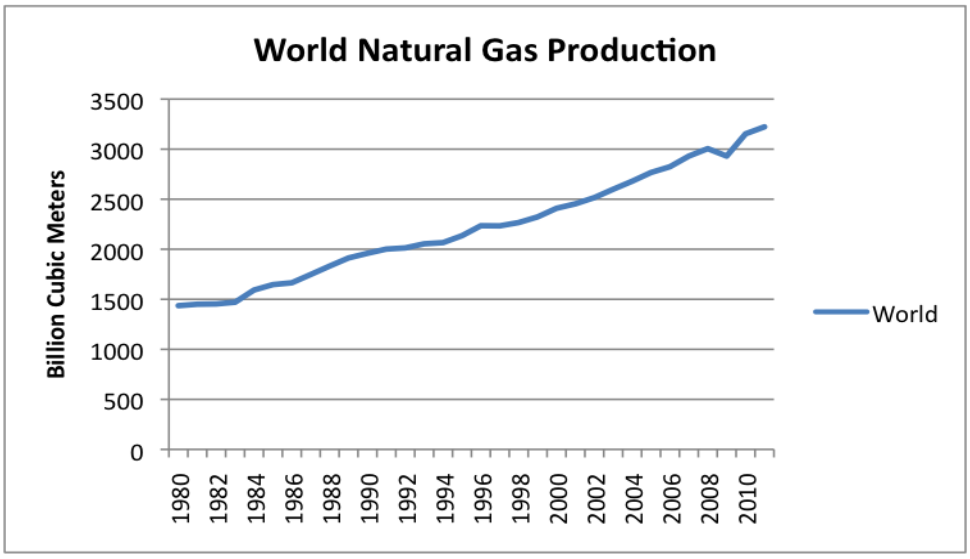

FIGURE 2-1 – World Natural Gas Production

(source : BP Statistical Review of World Energy Data,2012)

Generally, natural gas can be divided into two, which are sweet natural gas and sour natural gas. Huo (2012) stated that sour gas contain high amount of acidic gas usually CO_2 as well as hydrogen sulphide. International Energy Agency had report that 43% of world natural gas or 2,580 trillion cubic feet (TCF) resources excluding North America are sour. Russia proved to be the largest natural gas producer with around 1,700 trillion cubic feet (TCF) per year followed by Iran, Qatar and United States (IEA,2013). However, it is reported by International Energy Agency (2012) that Russia has 34% sour natural gas from total natural gas reserves of the country. Highest sour natural gas reserves in the world is at Middle East with 60% of the natural gas reserves are considered as sour (IEA,2010).

Table 2-1 below shows composition of natural gas reservoir in some parts of the world.

TABLE 2-1 : Composition of natural gas reservoirs in some parts of the world in volume percent basis (Rojey, 1997; Bahadori, Mokhatab et al. 2007; Bakar and Ali, 2010)

Component	**Reservoir**				
	Groningen (Netherland)	*Laeq (France)*	*Uch (Pakistan)*	*Uthmaniyah (Saudi Arabia)*	*Ardjuna (Indonesia)*
Methane	81.3	69	27.3	55.5	65.7
Ethane	2.9	3	0.7	18	8.5
Propane	0.4	0.9	0.3	9.8	14.5
Butane	0.1	0.5	0.3	4.5	5.1
Heavy Component	0.1	0.5	-	1.6	0.8
Nitrogen	14.3	1.5	25.2	0.2	1.3
Hydrogen Sulfide	-	15.3	-	1.5	-
Carbon Dioxide	0.9	9.3	46.2	8.9	4.1

Khesgi (2011) had stated that the most high concentration of CO_2 gasses contents occur in South East Asia. International Energy Agencies (2010) claimed that natural gas reserves at Erawan Field and Platong Field in Thailand contain CO_2 as high as 90%.

In Malaysia, most of the natural gas reserves is at Sarawak. Average content of CO_2 in natural gas fields in Malaysia varies from 28% up to 87% (IEA,2010). There are 15 offshore gas fields which contribute to 13.2 TCF up to date are undeveloped due to high content of CO_2 (Zahedi,2010). The amount of CO_2 content in the respective gas fields are present in table 2-2 below.

TABLE 2-2 – Amount of CO_2 content in respective gas field in Malaysia
(source : Petroleum and Policy Management PETRONAS, 2011)

Reserves Natural Gas in Malaysia				
Field	Total EUR (TSCF)	EUR Net of CO_2 (TSCF)	CO_2 Content	CO_2 Volume (TSCF)
Bujang	1.47	0.50	66%	0.97
Sepat	1.20	0.48	60%	0.72
Noring	0.58	0.23	60%	0.35
Inas	1.04	0.42	60%	0.62
Tangga Barat	0.33	0.22	32%	0.11
Ular	0.14	0.07	50%	0.07
Gajah	0.12	0.06	50%	0.06
Bergading	1.36	0.82	40%	0.54
Beranang	0.08	0.06	28%	0.02
Palas NAG	0.38	0.20	46%	0.18
K5 (Sarawak)	25.65	7.70	70%	17.95
J5 (Sarawak)	5.37	0.70	87%	4.67
J1 (Sarawak)	1.43	0.59	59%	0.84
T3 (Sarawak)	1.04	0.39	62%	0.65
Tenggiri	0.33	0.18	47%	0.15
Total	*40.52*	*12.62*	-	*27.9*

**EUR = estimated ultimate recovery*

2.2 Pre-Treatment of Natural Gas

CO_2 is known as one of the main contaminants present in natural gas feed. According to Safari et al. (2009), CO_2 need to be removed from natural gas before processing as it can corrode pipelines. CO_2, with the presence of water, will become acidic and can corrode or damage the pipelines as well as other equipment. Besides that, it also cause heating value of gas stream to be reduced significantly. The selling price of natural gas will be affected as it does not meet end user's sales gas specification (Darman and Harun,2006). When natural gas is cool down to very low temperature in order to convert it into Liquefied Natural Gas (LNG) for the storage and transportation purpose, CO_2 might be frozen and block the flows in pipeline system (Mukhtar, 2012). Due to all of that, it is vital for natural gas to go through pre-treatment section first in order to remove CO_2 from it. Basically, there are three different ways of removing CO_2 from natural gas which include separation with sorbents or solvents, cryogenics technique and membrane technique.

2.2.1 Separation Using Sorbents/Solvents

This separation technique involves adsorption/absorption with the regeneration unit. Figure 2-2 below shows pre-treatment section of natural gas.

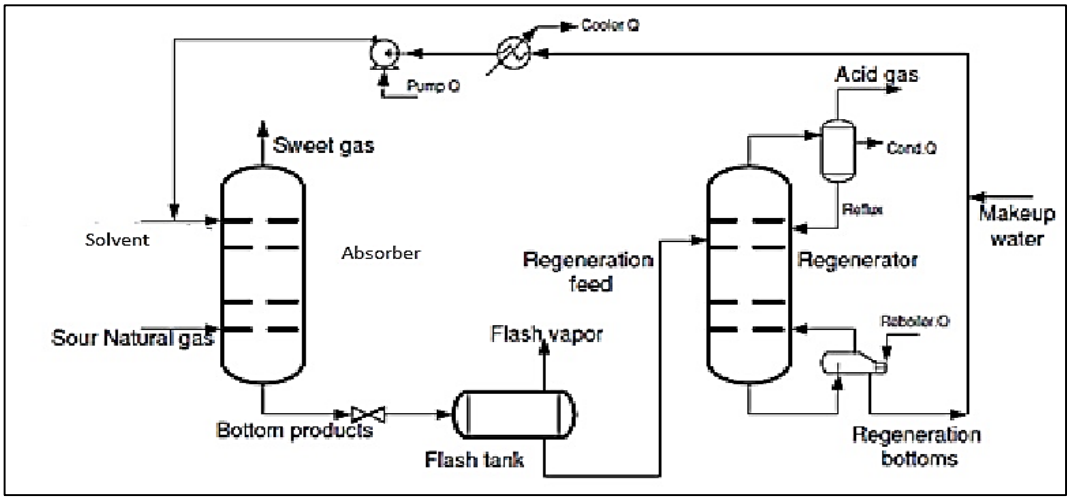

FIGURE 2-2 : Removal of CO_2 from natural gas involving absorption and desorption column *(Lunsford and Bullin,2006)*

Pre-treatment section also known as acid gas removal unit (AGRU). It involves absorption column and desorption column. Natural gas (mostly sour natural gas) is feed into absorption column in which CO_2 is absorb into solvent. In this absorption part, the natural gas (in gaseous phase) is contacted with liquid absorbent. This process occur countercurrently, in which liquid absorbent will enter from the top while natural gas enter from the bottom (Henley,2006). The solvent (absorbent) use in this process must have high gas solubility, high volatility, chemically stable, non-corrosive to the system, has no or very low effect to product as well as environment, low freezing point as well as low cost (Meyers, 2001). Usually, amine based solution is used for this purpose (Salako,2006).However, this amine treating processes have several drawbacks include large amount of regeneration energy, corrosive property that can induce equipment corrosive rate and degradation to organic acid (Henley,2006).

The natural gas free from CO_2 will go out at top of the absorber column while bottom product will be solvent rich in CO_2. The solvent rich in CO_2 need to be reused or regenerated (Salako,2006). Gas-liquid desorption process involved in desorption column in which the CO_2 will be removed from solvent rich in CO_2. Desorption process is the reverse process of absorption aims to recover the solvent. It is also known as regeneration (Lemmon et al., 2010). The solvent free of CO_2 will recycle back into absorber. Figure 2-3 below shows simplify block diagram of pre-treatment section of natural gas.

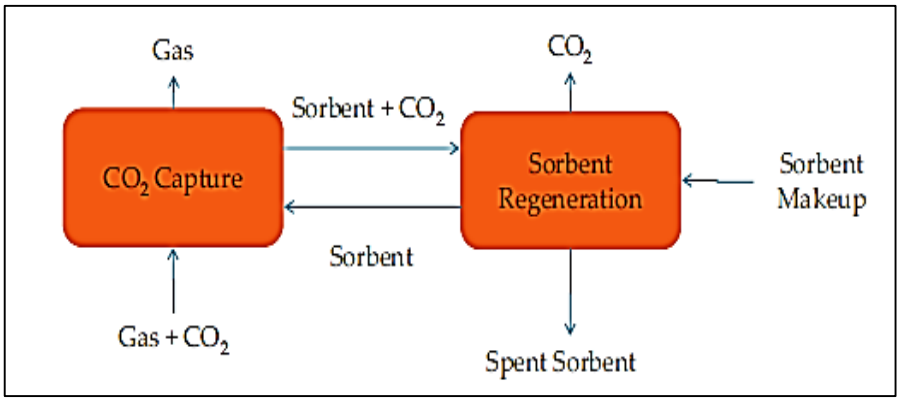

FIGURE 2-3 : Simplify block diagram of pre-treatment section of natural gas (Salako,2006)

For the adsorption the concept is same, however solid adsorbent is required. Usually, zeolite is used as because it can adsorb water and CO_2 effectively when it is cool

while release them when heated (James, 2012). When natural gas stream is bought into contact with solid adsorbent, there will be adhesion of several components due to the affinities with the adsorbent. The removing will occur either through chemisorption or physical adsorption (Simekit,2012). In chemisorption, there will be strong covalent bond formed between CO_2 with the adsorbent surface. The process is highly specific and irreversible. For the physical adsorption, it only involve weak Wan der Waals force. Due to the weak force, physical adsorption process required low energy compared to chemisorption, thus the adsorbent is easily regenerated (Meyes,2011).

According to Simone(2006), there are two different type of adsorption process use to separate CO_2, which are Thermal Swing Adsorption (TSA) and Pressure Swing Adsorption (PSA). In TSA, temperature is increase for the regeneration purpose by supplying heat. When temperature is high, adsorption equilibrium constant will decrease significantly, thus CO_2 can be removed (Meyers,2011). For the PSA, it involve increase in pressure during flowing of natural gas through the packed bed until concentration of the desired gas reached equilibrium. After that, the pressure is reduce by evacuation or depressurization aims for the regeneration (Wiley,2003).

2.2.2 Gas Separation Membrane

In membrane separation technique to remove CO_2, it use the concept of gas permeability. Gas is flow to the membrane through several different mechanism (Luebke et. al,2003). In this technique, only one component in the respective gas stream is allow to pass through faster than the other components.CO_2 will be removed accordingly due to the permselectivity of the membrane used ($Carmen$,2010). Figure 2-4 below shows basic principle of gas separation using membrane.

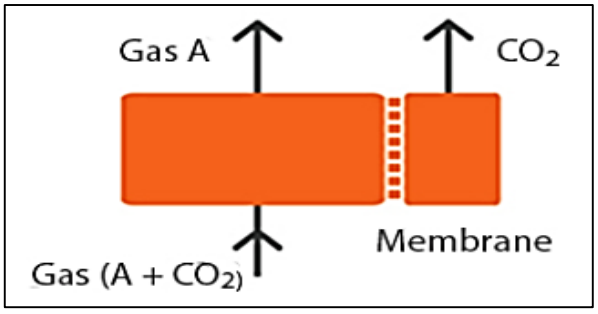

Figure 2-4: Separation of Gas using membrane
(Source : CO_2 capture project,2008)

Carmen (2010) and Yan (2007) highlighted disadvantage using gas separation membrane which are only applicable to medium size gas stream, currently cannot be used with the large scale of natural gas such industry thus cannot be compete with current absorption technique and also not economically feasible due to the pressure must be more than 450psig to operate effectively.

2.2.4 Cryogenic

Cryogenic is another way to remove CO_2 from natural gas in pre-treatment section. It is also known as low temperature distillation because the process need very low temperature. Figure 2-5 below the basic principle of separating CO_2 from natural gas using cryogenic technique.

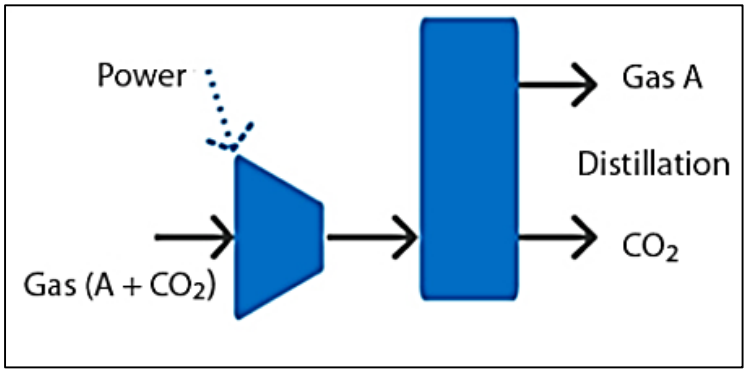

Figure 2-5: Cryogenic Process
(source of picture: CO_2 capture project,2008)

In this process, turbo expander is used to bring down gas temperature. Result from the cooling and condensation, CO_2 will change state into liquid and will be separated. (Tobin, 2006). However, cryogenic known to be used only with the natural gas stream that had CO_2 more than 90%. It will be less efficient to be used when concentration of CO_2in gas stream is low. The disadvantages include energy needed to cool down the gas is very high especially when amount of CO_2 is low and high tendency for blockage to occur in the process equipment (Carmen,2010).

This research paper is focussed on first technique being describe which is absorption and desorption technique to remove CO_2. Desorption column (regeneration unit) will become main concerned here.

2.3 Desorption Column / Regeneration Unit

As stated, after absorption section, absorbent rich in CO_2 will go to desorption column or regeneration unit. In the desorption column (packed tower), the liquid absorbent rich in CO_2 will enter the column from the top. The stripping agent will enter from the bottom. When they meet counter-currently, absorbed CO_2 will released into gas phase. This will leaves absorbent free from CO_2 and can be used again for absorption purpose (McCabe et. al, 2005). Refer Appendix A for internal view of packed column.

However, Alie et al. (2005) and Yan et al. (2007) stated that this technique involve high operating cost and large energy consumption. The temperature for regeneration of the absorbent usually will go beyond 120℃, thus there will be probability of inevitable thermal degradation of the absorbent (Versteeg et al., 2011).

James and Henry (2007) realized the drawbacks of the absorption and desorption column using mono-ethanolamine (MEA) to remove CO_2 and regenerate the absorbent. Thus they conducted research in order to increase the efficiency of the whole process. From their research, they claimed that sterically hindered amine, 2-amino-2- methyl-1-propanol can be regenerate more easily and effectively. However, the absorption is less efficient than MEA.

There are also many researchers try to come out with blended absorbent that needs low regeneration energy. This blended absorbent includes KS serials and piperazine (PZ) solvent. According to Rochelle (2006), this blended solvent has absorption rate around 30% faster than MEA. Freeman (2009) also claimed that blended absorbent KS serial and PZ solvent has loading capacity 10% more than MEA with energy requirement lower than MEA by 5% in approximate.

Gary et al. (2007) through their experiment claimed that the best configuration to be used with PZ solvent is by using double matrix stripper together with double intercooler absorber. They also stated that loaded PZ solution can resist thermal degradation better than MEA, thus supporting the statement made by Rochelle (2006). PZ solution can stand up to temperature 135℃ before degradation (Gary et. al,2007). However this novel solvent are very expensive. In order to minimize the losses due to the high prices of solvents, the natural gas pre-treatment section need to modify into multi pressure stripping. The overall

process will become more complicated, thus not feasible to be used in real industry (Freeman et al., 2009).

Rahman et al. (2010) analysed ionic liquid to be used as solvent. It is known that ionic liquids can dissolves CO_2.Advantages of this ionic liquids as stated by Rahman (2010) is that it is stable even at high temperature. Heat energy required for regenerate also lower compared to MEA and KS/PZ solvents. However, ionic liquid is more expensive compare to KS and PZ serials solvent studied by Gary et. al (2007) and Freeman (2009). It is also more economic sensitive to impurities as well as process upset (Rahman et al.,2010).

Besides research to change the absorbent/solvent used with the one with low regeneration energy, there are also research done on modified stripping process in order to reduce energy consumption at regeneration stage. Oyenekan and Rochelle (2007) develop four innovative stripper configurations which aims to reduce operating cost by lowering the energy requirement. This includes matrix stripper, stripper interheating, flashing system and multi-pressure stripping.

In matrix stripper, the absorbent rich in CO_2 is divide or split into two different streams. The first one will be directed to the first stripper while the second will be directed to the top of the second stripper. This occur at high pressure (Oyenekan, 2007). With this matrix stripper configuration, the compression required at the downstream is lower compared to conventional ones. Despite the two configurations of matrix stripper, three configurations also can be used to get better outcomes (Rochelle,2007).

For the modified multi-pressure stripping, it involves several increment in pressure. In this system, vapour streams that exiting lower-pressure stripper will be compressed and then entering next higher pressure stripper segment. The reboiler duty will be lower compared to normal stripping process (Oyenekan and Rochelle,2007). Oyenekan (2007) also reported that there is way to upgrade this multi-pressure stripping, that is by using it with split streams. Through this, loss of work can be decreases significantly (Fisher,2007). However, this new configuration is complicated.

Oyenekan and Rochelle (2007) claimed that from four different stripper configurations they had studied, matrix stripper showed the best performance in overall. It can generally reduce energy required for regeneration for about 5% to 15% average. Matrix stripper configuration can reduces compression work. This is as a result of large

portion of the CO_2 is stripped at higher pressures (Fisher,2007). However, the process flowsheeting become more complicated. Refer Appendix B for process flowsheeting proposed by Oyenekan and Rochelle (2007).

Wagener and Rochelle (2011) further the research conducted by Oyenekan and Fisher (2007). They worked on modified stripping and had simulated five different stripper configurations. This configuration consist of 1-stage flash, simple stripper, stripper with adiabatic lean flash, 2-stage flash and interheated column. This study proved that to reduce the energy consumption of the process, interheated column give best the performance compare to other four configurations. Through interheated column configuration, energy consumption successfully reduced by 11% (Wagener,2011). However, just like matrix stripper, this modified configuration make the process become more complex, thus increase total capital cost and not economically feasible to be applied (Rochelle,2011).

Recently, Wang et al. (2012) studied on the use of membrane vacuum technology for desorption of dissolve CO_2 in solvent. It is noted that when membrane vacuum regeneration is run in long term, there is a risk of membrane wetting to increase as a result of increase of membrane pore size. (Fang,2012). Yan et al. (2012) had conducted research on membrane technology by targeting to get low energy consumption during the regeneration process. Before that, Li and Chen (2005) already reported that membrane technology can be used as alternative to current desorption column for desorption of CO_2. However, study on this is still limited and result is uncertainty up to date.

2.4 Concept of Flow through Nozzle and Bernoulli Equation

Currently, in industry, desorption of CO_2 is done using desorption packed column. This column has two openings. Gas and liquid streams will enter the column counter-currently. The desorption of gas from loaded solvent will occur (Harriot et al,2005).

However, in this project, converging nozzle (different diameter at inlet and outlet) will be used as equipment in desorption of dissolved CO_2. Concept of pump cavitation is applied in which pressure on portions of the liquid will lowered enough for the liquid to change states to gas. During this stage, bubbles will formed and collapse. Desorption of gas will occur consequently (Uhlman,2011).

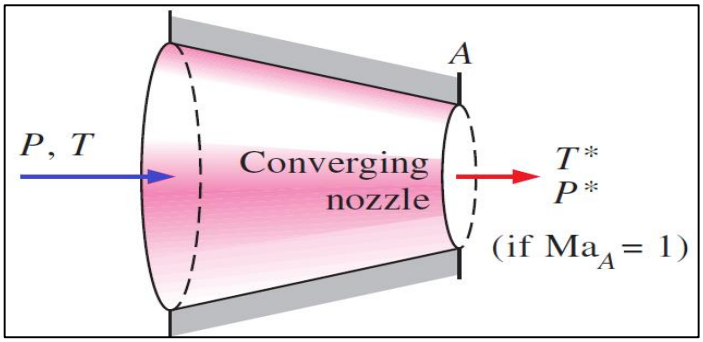

FIGURE 2-6 : Flow through converging nozzle
(source of picture :Wagener(2011), Nozzle Applet)

Figure 2-6 shows flow through the converging nozzle. According to Wagener and Rochelle (2011), through the nozzle, velocity of the fluid will increase when cross sectional area decrease. Wagener and Rochelle (2011) also explained the pressure drop across the nozzle through Bernoulli Equation in which pressure will be lower at the end of nozzle compared to at inlet due to high velocity of fluid.

$$z_1 g + \frac{{v_1}^2}{2} + \frac{p_1}{\rho} = z_2 g + \frac{{v_2}^2}{2} + \frac{p_2}{\rho} \qquad (Bernoulli\ Equation)$$

Figure 2-7 below show how pressure changes along the flow in expansion nozzle.

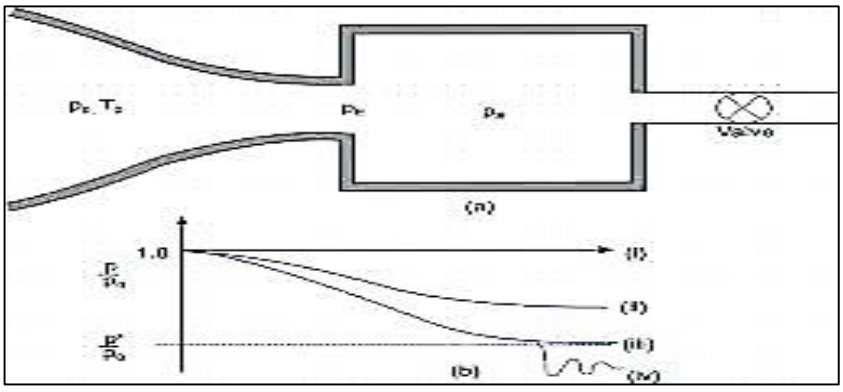

FIGURE 2-7 : Changes of pressure along the flow through nozzle
(source of picture : Wagener(2011), Nozzle Applet)

Decrease in pressure occurred when velocity increase (Uhlman,2011). When liquid is bring to a point in which it is low enough for the liquid to changes state into gas, cavitation will occur (Randall & Whitesides, 2012).

2.5 Equilibrium and Non-Equilibrium System

To understand the concept of gas in liquid (CO_2 gas in water), the concept of equilibrium and non-equilibrium need to be understand first. Smith, Van Ness and Abbott (2008) from their book "Introduction to Chemical Engineering Thermodynamic" explain the equilibrium system as the system that does not possess any change. In other words, if there is no change in the system, the system is in equilibrium.

According to Smith (2008), in equilibrium condition, the system is static. In the macroscopic properties, there will be no changes occur. This can be achieved through times (Abbott, Smith & Van Ness,2008). Spring and Coa (2012) stated that equilibrium system can be imagine as an isolated system in which there will be no change at all due to the forces which are in exact balance.

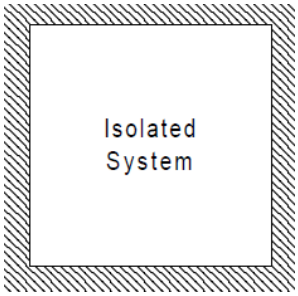

FIGURE 2-8 : Equilibrium system to be imagine as isolated system
(source : Cao(2012). *Equilibrium versus Non-Equilibrium*)

For the liquid and vapour phase in contact, the pressure, temperature and composition will eventually come to a constant value with time. When the system reached this condition, it is known to be reach the equilibrium (Abbott, Smith & Van Ness,2008). Before all the properties reach constant final value, it will keep changing with time. This condition referred to non-equilibrium condition. In order words, any system which is not in equilibrium can be describe as non-equilibrium condition (Spring, 2012).

2.6 Carbon Dioxide in Water Equilibrium

It is known that when gas come into contact with water, some of it will be dissolved. This is highly depends on temperature and pressure of the gas (Cosmos,2013).

Same goes to the carbon dioxide (CO_2). When come into contact with water, CO_2 dissolve in the water (H_2O). Researchers agreed that the solubility of CO_2 in water goes up to $90cm^3$ per 100mL of water at room temperature. CO_2 dissolved in water, thus change from gas phase to the aqueous phase as in chemical equation below.

$$CO_2(g) \leftrightarrow CO_2(aq).$$

Elhajj, Azizi, and Al-Hindi (2013) stated that when CO_2 dissolved in water, it will undergoes three chemical equations. The first one known as CO_2 hydration as follows:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3$$

According to Zhang (2011), this hydration reaction is kinetically slow. The dissolved CO_2 form carbonic acid (H_2CO_3) when react with water. Following Henry's Law, at low moderate pressure, ideal equilibrium condition between aqueous and gaseous phase is as in equation below.

$$\frac{C^*_{H_2CO_3}}{P_{CO_2}} = H_{CO_{2,0}} = \frac{C^*_{H_2CO_3}}{y_{CO_2}P}$$

Where, $H_{CO_{2,0}}$ = Henry's coefficient of CO_2 in pure water

P_{CO_2} = partial pressure of carbon dioxide

$C^*_{H_2CO_3}$ = concentration of physically dissolved CO_2 and H_2CO_3 in equilibrium

Zhang (2011) stated that the carbonic acid will then dissociates to bicarbonate, ${HCO_3}^-$ as well as carbonate, ${CO_3}^{2-}$ as in equations at below.

$$H_2CO_3 \leftrightarrow {HCO_3}^- + H^+$$

$$HCO_3^- \leftrightarrow {CO_3}^{2-} + H^+$$

Water can dissociate itself and form H^+ and OH^-ions (Wang & Lawal, 2011). This OH^-can be react with CO_2 as follows:

$$CO_2(aq) + OH^- \leftrightarrow HCO_3$$

Above equation known as hydroxylation reaction and it is significance at pH more than 7.0 (Zhang,2011).

2.7 Solubility of Carbon Dioxide and Effect of Temperature

2.7.1 Solubility CO_2 in H_2O

When gas is dissolved in a fluid, the solubility will be limited by equilibrium between the gas itself with the saturated solution of the gas. "Equilibrium is defined as static condition in which there will be no changes occur in the system with time" (Smith,2005).

It is known that solubility of CO_2 in water will be depending on temperature and also the pressure (El Hajj et al,2013). There are many published data about the solubility of CO_2 in water. Figure 2-9 below shows graph of changes of CO_2 solubility in water according to temperature and pressure.

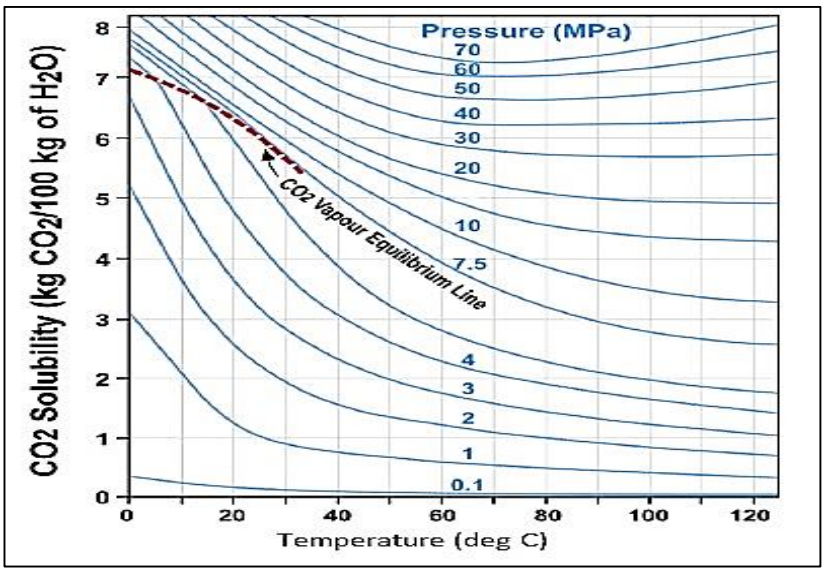

FIGURE 2-9 : Solubility of CO_2 in pure water (Shapley,2013)

Graph in figure 2-9 shows that when pressure of CO_2 increase, solubility of CO_2 in the water will also be increases. Unlike the effects of pressure, temperature will give inverse effect in which increasing temperature will decrease solubility of CO_2 in fluid (Cosmos,2013). This statement is correct up pressure temperature 65℃ and pressure 30MPa. Above this temperature and pressure, solubility of CO_2 will increase again (Shapley,2013). Refer Appendix C for CO_2 solubility data over wide range of temperature and pressure.

2.7.2 Henry's Law

Solubility of CO_2 always following Henry's Law. According to Smith and Abbott (2005), Henry's Law stated that "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid"

$$\text{Henry's Law : } y_i = x_i H_i$$

Where $H_i = Henry's\ constant$

$x_i = mole\ fraction\ of\ component\ i\ in\ liquid$

$y_i = mole\ fraction\ of\ component\ i\ in\ vapor$

According to Larryn and Nikolay (2003), for the solubility of CO_2 in water, Henry's Law need to be modified by adding fugacity and activity coefficient as follow:

$$x_{CO_2} = \frac{f^0{}_{CO_2} y \gamma_y}{H_i \gamma_{CO_2}}$$

Where $H_i = Henry's\ constant$

$x_{CO_2} = mole\ fraction\ of\ CO_2\ in\ aqueous\ phase$

$y = mole\ fraction\ of\ CO_2\ in\ non-aqueous\ phase$

$f^0{}_{CO_2} = fugacity\ coefficient$

$\gamma_{CO_2} = activity\ coefficient\ of\ aqueous\ CO_2$

$\gamma_y = activity\ coefficient\ \ in\ non-aqueous\ phase$

(source of equation : Larryn & Nikolay (2003). Fluid Phase Equilibria)

According to Carroll and Slupsky (1991), Larryn and Nikolay (2003) and Bala (2005), at low pressure the activity coefficient can be ignore. Carroll, Slupsky and Mather (1991) had compile result of experiments from several authors and plotted the graph of Henry's constant for CO_2 in water as in figure 2-10 next page.

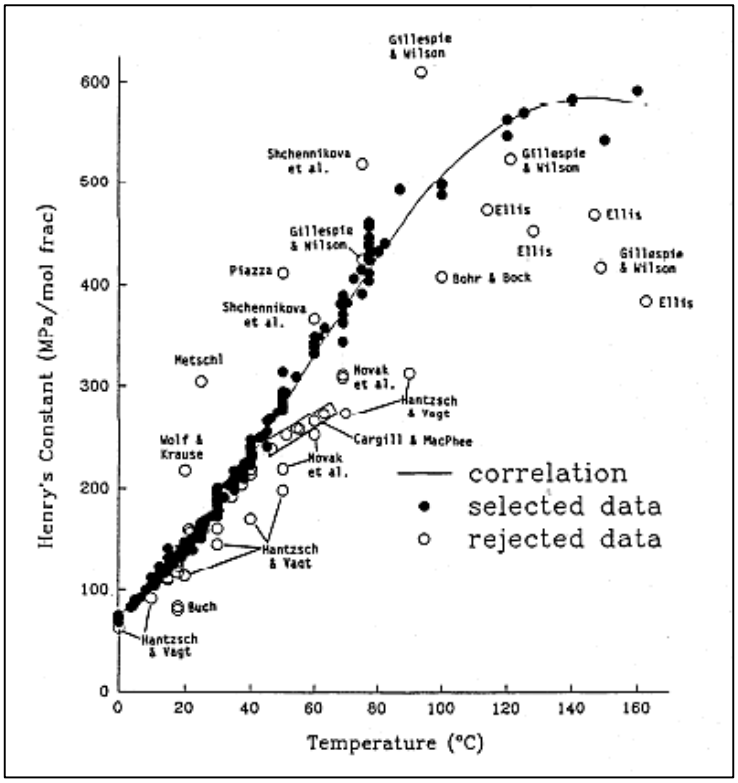

FIGURE 2-10 : Graph of Henry's Constant for CO_2 in H_2O
(source : Carroll, Slupsky & Mather (1991).Physical Chemistry Ref. Data Vol. 20)

2.7.2 Equation of State

Basically, non-ideality of gas describe by Equation of State (EOS). As at high pressure ideal gas is no longer accurate, EOS is used to increase the accuracy. EOS relates thermodynamics properties of a system including pressure and temperature (Elhajj,2014). EOS includes van der Waals equation (vdW), Redlich-Kwong equation (RK), Soave-Redlich-Kwong equation (SRK) and Peng-Robinson equation (PR). Bala and Gainar (2005) suggest to use RK to calculate fugacity of CO_2.

2.8 Physical Desorption and Desorption Kinetics

Desorption is actually opposite of absorption and sometimes known as stripping. According to Copeland et al. (2001), desorption refers to phenomenon in which substance is release through or from the surface (Wong,2011). Rate of desorption. R_{des} according to Tobiessen (2008) is as follows:

$$R_{des} = kN^x$$

Where $k = rate\ constant\ for\ desorption\ process$

$$N = surface\ concetration\ of\ absorbed\ species$$

$$x = kinetic\ order\ of\ desorption$$

Rate constant for desorption process is temperature dependent, thus following Arrhenius equation as follows

$$k_{des} = Ae^{-\frac{Ea}{RT}}$$

For desorption of gas from liquid, Henry's Law is applicable. According to Hamborg and Versteeg (2012), desorption gas from liquid governed by two factors which are mass transfer and kinetics. In this research project, the main focus is physical desorption. Physical desorption is the process of desorption through physical mean which does not involve activation energy (Copeland et.al,2001). For the physical desorption of CO_2,it is based on solubility of CO_2 in the solvent. This effected by partial pressure and temperature (Versteeg,2012).

2.9 CO_2 Loading

CO_2 loading in water is described as moles of CO_2 per moles of water and it is usually denoted as α_{CO_2}(Hamborg & Versteeg,2012). According to Jamal et. al. (2006), CO_2 loading gives significant effect on equilibrated partial pressure of CO_2. Change in CO_2 loading when running the test will resulted in initial and infinite equilibrated CO_2 partial pressure. Ramachandran et al. (2006) through their experiment on kinetics of CO_2 absorption claimed that increases in CO_2 loading will decrease the mass transfer. CO_2 loading can be portrayed by solubility of CO_2 and its significantly effect by temperature. The higher the temperature of the solution, the lower the solubility of CO_2. (Florin et al.,2007).

2.10 Research Gap

Table 2-3 below summarized research done for the regeneration unit

TABLE 2-3 : Research Gap on Regeneration Unit

Year	Author	Research Area / Finding
2005	McCabe et al	Desorption CO_2 using packed column – countercurrent flow
2005	Alie et al	Regeneration unit – large energy consumption and operating cost of desorption column is high
2007	Yan et al	Supporting idea of Alie et al – drawback of desorption column
2007	James and Henry	Absorbent liquid that can regenerate more easily (amine, 2-amino-2- methyl-1-propanol)
2007	Oyenekan and Rochelle	Modified stripping process aims lowering cost of regeneration absorbent – matrix stripping configuration give the best performance, however the flowsheeting is complicated
2009	Freeman et al	Lowering regenerating energy by using blended absorbent KS serial and PZ solvent – expensive and not economically feasible
2010	Rahman et el	Analyse ionic solvent as absorbent – expensive and not feasible
2011	Wagener and Rochelle	Modified stripping process using five different stripper configuration – interheated column give the best performance, however capital cost is increasing due to complexity
2012	Wang et al	use of membrane vacuum technology for desorption of dissolve CO_2 in solvent – still new to develop

From table 2-3, it can clearly be seen that many researchers try to minimize the cost and regenerating energy used. The research done on absorbent itself and also on the process of desorption of CO_2. However, most of the research results in increasing capital cost as well as increasing complexity of the process. None of the research done aims to change the desorption column itself with other technique that can remove CO_2 instantaneously.

As this research project focussed on effect of temperature on desorption of CO_2 from water, summarize for the previous research related to absorption and desorption of CO_2 in water is present in table 2-4 below.

TABLE 2-4 : Research Gap for CO_2 in water system

Year	Author	Research Area / Finding
1991	Carroll, Slupsky & Mather	Assemble all experiment data for solubility of CO_2 in water. Point out disagreement of data especially at high pressure. Result in published of correlation between temperature and Henry's constant for CO_2 in water.
2003	W. Diamond & N. Akinfiev	Study on solubility of CO_2 in water with wide range of temperature ($1.5℃ - 100℃$) and pressure (0.1 MPa to 100 MPa). Result in developing thermodynamic model of solubility of CO_2 in water with 1 standard deviation (1.7%) from experimental data.
2005	Bala & Gainar	Make estimation of the Henry's constant at high pressure. Compare experimental data with Krichevsky-Ilinskaya equation and proved the agreement between the value
2012	Hamborg & Versteeg	Study on mass transfer rate for absorption and desorption. Proved that chemical reactive absorbent effect mass transfer rate of absorption and desorption up to certain point.
2014	Elhajj, Al-Hindi & Azizi	Make a critical review on absorption and physical desorption of CO_2 in water system using several different types of contactor. They claimed that mass transfer coefficient will be varies with the hydrodynamic and configuration of the system itself.

To change desorption column into other technique, knowledge on desorption is crucial. Table 2-4 shows several research on CO_2 in water system. There are many others published research related to the CO_2 in water. As can be seen in the table, early study involve solubility of CO_2 and Henry's constant then trend change to the absorption and desorption. However, research focussing on physical desorption of CO_2 very limited up to date, thus this become the motivation to study that area.

CHAPTER 3

METHODOLOGY

This chapter describes methodology of the research project, key project milestone and the Gantt chart towards completing the project.

3.1 Research Methodology and Project Works

The methodology is planned accordingly so that amount of CO_2 desorb from water by using physical mean can be measure and record and effectiveness of desorption using converging nozzle by varying the temperature can be determined. This is in line with the objectives of the project as stated in Chapter 1.

For the laboratory experiment, test rig consists of water tank (300L) equipped with heater and thermocouple, converging nozzle for the desorption process, pressure vessels (absorption and desorption tanks) , pump and compressor are used. Other equipment used include sampling collector (20mL capacity) equipped with pressure chamber (pressure bomb), beaker and 50mL and 10mL of measuring cylinder for the collecting of the sample and determination of the volume of carbon dioxide. The pressure vessels (absorption tanks) are covered with insulator to minimize heat losses. For the chemical, carbon dioxide gas and water are used. Water is used as physical solvent.

Simplify block diagram for the setup of equipment is as shown in figure 3-1 next page. Referring to the block diagram, water in the water tank need to be heated up to the desired temperature first. Then the water will be pump into absorption tanks (pressure vessels). The CO_2 gas from the supply will be compress to the absorption column at desired pressure. Absorption process will take places here. After that, the water rich with CO_2 will be directed to the converging nozzle that have different internal diameter in which desorption will occur. The result is collected at the third pressure vessel (desorption tank).

Refer Appendix D for clear view of complete flow diagram of the setup of experiment and Appendix E for the picture of equipment and some important parts of it.

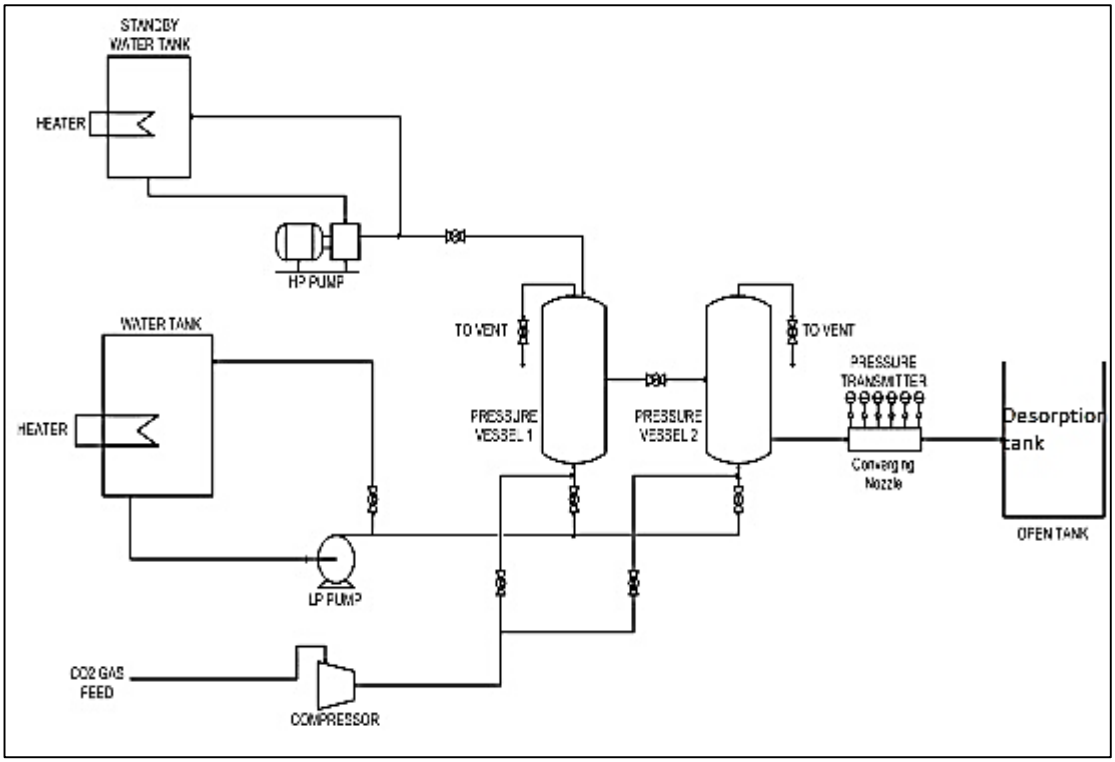

FIGURE 3-1 : Simplified Block Diagram for the setup of experiment

Refer Appendix D for the clear view of the flow diagram of test rig used.

Basically, in this experiment, the initial CO_2 loading is kept constant throughout the experiment that is 0.001 mol CO_2/mol H_2O. By calculation, 0.001 mole fraction of CO_2 will give 30mL of CO_2 in 20mL water sample used. Procedure to run the laboratory are as follow:

Procedure for Experiment (initial mole fraction of CO_2 constant at 0.001 ($30mL$))

i. Turn on main switch of the test rig (equipment).

ii. Fill the water tank with water. Adjust the temperature of the water to be at 40℃ (use automatic temperature controller).

iii. Open valve (BV-1011) that direct the pipe from water tank to the absorption tanks (pressure vessel 1 and 2). Turn on the low pressure pump.

iv. Pump water into absorption tank 1 and absorption tank 2 until level indicator shows water level is at maximum. Check the temperature of water in the absorption tanks to ensure that it is same with the temperature set early. Noted that the absorption tank 1 is only for the backup but still need to be feed to maintain pressure in tank 2.

v. Open the valve at the pipe carrying gas supply (BV-2001,BV-2005 and BV-2008). Switch on the compressor.

vi. Open gas inlet valve (BV-3013 and BV-3011). Pump in CO_2 gas into absorption tanks. Adjust the compressor until pressure in the absorption tank reach desired pressure (15 bar).

vii. Fill a beaker with water. Invert 50mL measuring cylinder fill with water and immersed it in the beaker. Make sure there is no air bubble trap inside the measuring cylinder.

viii. Take the sample from sampling point at absorption tank using sampling collector equipment equipped with pressure bomb for every 15 minutes. Direct the CO_2 gas collected by pressure bomb into inverted measuring cylinder prepared early in step vii.

ix. Record the volume of CO_2 gas collected. To continue to the next step, make sure that the volume of CO_2 gas collected is $30mL$ (0.001 $mol\ CO_2/mol\ H_2O$). If the amount of CO_2 is less than $30mL$, wait for another 15 minutes and take another samples. Noted that the amount of CO_2 collected here is the initial amount CO_2 absorbed into the water which need to be keep constant.

x. After initial sample is recorded, switch on high pressure pump 2 and set it with desired operating pressure (15 bar). Switch on the solenoid valve.

xi. Water rich with CO_2 gas will automatically be direct to the converging nozzle (0.5 inch at one end and 0.25 inch internal diameter at other end) and desorption process occur instantaneously.

xii. Water will be collected at desorption tank. Take the sample at sampling point before water fill in the desorption tank (sampling point is at the outlet of the converging nozzle).

xiii. Record the amount of CO_2 gas collected (the method to collect the sample is same as stated at step vii and viii except that 10mL measuring cylinder is used).

xiv. The water from all the tank is drain out by opening drain valve (BV-3015, BV-3012 and BV-4012). The pressure is relief by opening pressure relief valve.

xv. Repeat the experiment with different temperature (323K, 333K, 343K, and 353K) with constant pressure at converging nozzle

xvi. Repeat the experiment for three times

In order to achieve objectives of the research project, amount of CO_2 that successfully desorb from water and how temperature effect the trend of desorption of dissolve CO_2 in water need to be analysed. Efficiency at different temperature is determined by comparing amount of CO_2 release with the amount of CO_2 at vapour liquid equilibrium at 1 bar (explain in discussion section next chapter). This set of experiment need to be repeat for three times for better accuracy. The absorption process part is not proceed until equilibrium be achieved.

3.2 Key Milestones

Figure 3-2 below shows key milestone towards completing this project while table 3-1 and 3-2 next page shows work done in Gantt Chart form.

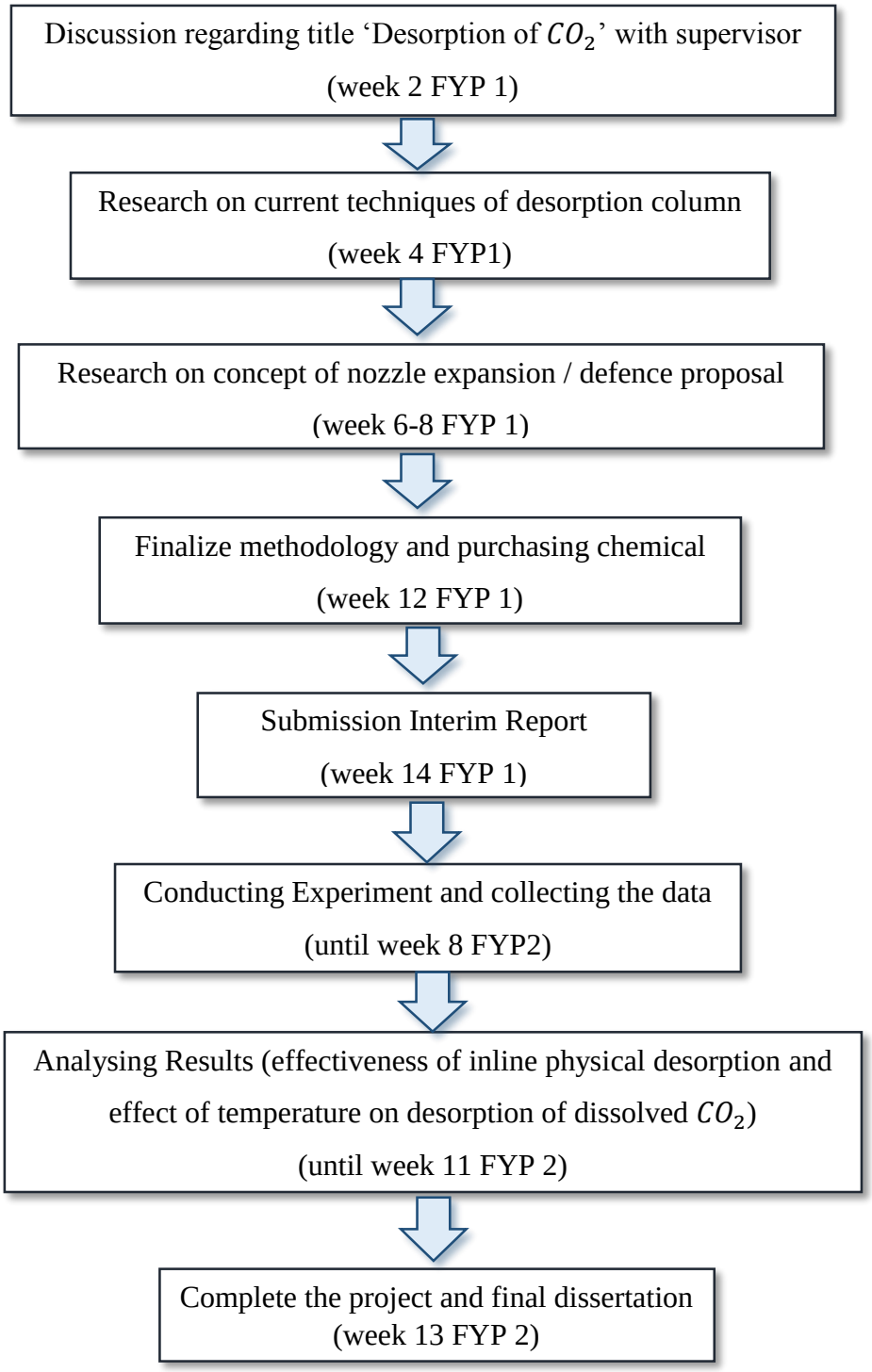

FIGURE 3-2 : Project Key Milestones

3.3 Gantt Chart

TABLE 3-1 : Gantt Chart for FYP 1

No	Detail/week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Review FYP title														
2	Literature analysis (current desorption process)														
3	Find out problem statement, objectives to be achieve and propose methodology														
4	Proposal defence														
5	Finalize methodology on how to test desorption by varying temperature														
6	Purchasing chemical and booking laboratory														
7	Complete the proposal and submission of interim report														

Process

TABLE 3-2 : Gantt Chart and Key Milestone for FYP 2

No	Detail/week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Conduct the desorption experiment using test rig and collect the data (vary *temperature*)														
2	Submission progress report														
3	Analysing results (graph relationship of temperature with desorption)														
4	Analysing results (effectiveness of desorption)														
5	Submission dissertation and technical paper														

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents the outcomes from the experimental works done. All the outcomes are critically analysed and being discussed in detail throughout this chapter. Towards the end of the chapter, effect of temperature towards desorption of dissolved CO_2 from water and also efficiency of desorption using converging nozzle clearly be convey.

4.1 Results and Discussion

4.1.1 Effect of Temperature towards Desorption of CO_2

One of the objectives of this research is to investigate effect of temperature towards desorption of dissolved CO_2 from water using converging nozzle. In the laboratory work done to show how temperature affect desorption, the initial amount of CO_2 absorb in water is kept constant at mole fraction 0.001 $mol\ CO_2/mol\ H_2O$. By calculation, mole fraction 0.001 will give volume of $30mL\ CO_2$ in 20mL water sample. In order to get same amount of CO_2 gas dissolved in water at different water temperature, time for the absorption process is vary. When running the desorption part, pressure is set to be constant at 15bar throughout the experiment. This is to ensure that result shows only reflect the effect of temperature without being disturbed by other parameters. Experiment is repeated for three times to increase reliability and accuracy of the data recorded.

Mole fraction is calculated based on volume of CO_2 (mL) per 20mL of sampling water. Mole fraction is used throughout the discussion instead of volume for easy explanation and understanding. Noted that when collecting the sample, CO_2 is released to the atmospheric pressure (1 bar), not to the vacuum. Thus not all amount of CO_2 in water is collected in the measuring cylinder. At atmospheric pressure, some of the CO_2 still dissolved in the water. When calculating mole fraction of CO_2, the amount of CO_2 that are still dissolved in water at 1 bar is taken into account and be added with the amount of CO_2

collected in measuring cylinder. This gives the actual amount of CO_2 that need to be recorded and analysed.

In this experiment, basically, desorption occur when water rich with CO_2 flow through converging nozzle. Converging nozzle used has larger cross sectional area at the inlet compare to the outlet (0.5 inch internal diameter at one end (inlet) and 0.25 inch at the other end). When the water flow through the converging nozzle, pressure drop occurred. This is shown by the pressure indicator in which at inlet of the converging nozzle, the pressure recorded is 15 bar (as set). When water flow throughout converging nozzle, pressure drop to 10.49 bar, 8.41 bar and lastly to 6.3 bar at the end of converging nozzle (outlet). As the result of pressure drop, nucleation is formed, thus desorption process occur.

This phenomenon can be explain through mass balance and continuity equation, in which when fluid flow from large cross sectional area to small cross sectional area, its velocity increase (Geankoplis, 2005). According to the Bernoulli equation, as velocity at one end increase, its pressure will be decrease accordingly. This explain how the pressure drop occur throughout converging nozzle. If pressure drop is high enough, bubble nucleation will be form and desorption process occur (Chakrabarty,2008). Refer page 14 for Bernoulli Equation. This explain working principle of the converging nozzle use to remove dissolved CO_2 from the water (solvent).

Table 4-1 next page shows mole fraction of CO_2 in water right after desorption process take place at converging nozzle for all the three runs of the experiment. Appendix F can be refer for the amount of CO_2 in term of volume per 20mL of water sample (before convert into mole fraction). From the table, it can be see that mole fraction of CO_2 in water decrease from 0.00068 to 0.00040 in average when temperature increase from 313K to 353K. Basically, reduce in mole fraction from initial mole fraction of CO_2 in water indicates that CO_2 being release and desorption process take place. As initial mole fraction of CO_2 is constant at 0.001 mol CO_2/mol H_2O , the lower mole fraction of CO_2 after desorption show that more CO_2 had being desorbed.

In order to see clearly the trend of decreasing of mole fraction of CO_2 in water after desorption process take place for all of experiments run, graph of mole fraction of CO_2 in water after desorption was plotted in figure 4-1 page 32.

TABLE 4-1 : Mole fraction of CO_2 after desorption

Temperature (K)	**Pressure (bar)**	**Mole fraction of CO_2 after desorption** *(mol CO_2/mol H_2O)*			
		1st run	***2nd run***	***3rd run***	***Average***
313	15	0.00068	0.00067	0.00069	0.00068
323	15	0.00058	0.00058	0.00057	0.00058
333	15	0.00049	0.00050	0.00050	0.00050
343	15	0.00044	0.00043	0.00043	0.00044
353	15	0.00042	0.00040	0.00039	0.00040

**initial mole fraction of CO_2 kept constant at 0.001 mol CO_2/ mol H_2O*

Based on graph of mole fraction of CO_2 in water after desorption against temperature in figure 4-1 next, it can be say that all the three experiments run show same effect of decreasing mole fraction of CO_2 in water after desorption. Even though initial mole fraction of CO_2 is constant at 0.001 mol CO_2/ mol H_2O, the final mole fraction (after desorption) is vary at different temperature in which increase in temperature give lower mole fraction of CO_2 compare to at low temperature. This indicates that the amount of CO_2 desorbed increase when temperature increase.

As stated early, desorption occur as the result of bubble formation when water rich with CO_2 flow through the converging nozzle. When temperature increase, bubble formation will be increase, thus more CO_2 will be desorbed. Increase in amount of CO_2 desorbed from water result in low mole fraction of CO_2 remain in water after desorption. This follow the prediction made by Talanquer and Oxtoby (1995). According to prediction of these authors, temperature give effect on bubble formation in which more bubble are expected to form when temperature of the binary fluid is high compare to when temperature is low.

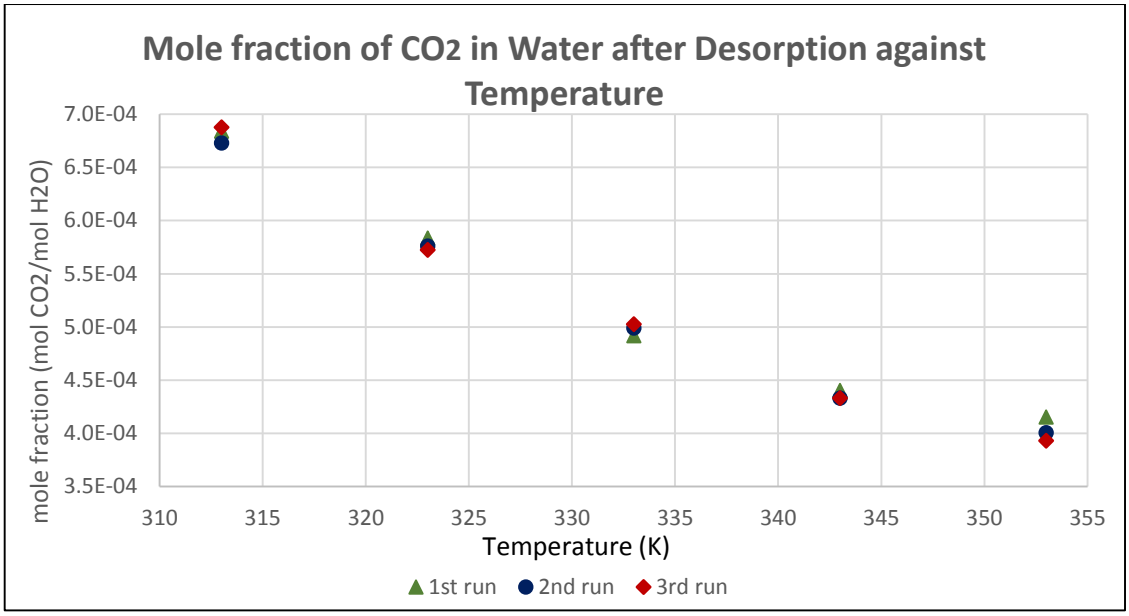

FIGURE 4-1 : Graph of mole fraction of CO_2 in water against temperature

To see more clearly how temperature affect desorption given constant CO_2 loading and pressure, graph of mole fraction of CO_2 desorbed against temperature is plotted as in figure 4-2 next page. Graph is plot based on average value from all the three experiments run. Amount in term of mole fraction of CO_2 in water desorbed from water can be determine by the difference between initial mole fraction of CO_2 dissolved in water which is 0.001 with the mole fraction of CO_2 in water after desorption process occurred.

$$Mole\ fraction\ of\ CO_2\ in\ water\ desorbed$$

$$= Inital\ mole\ fraction\ of\ CO_2\ in\ water - final\ mole\ fraction\ of\ CO_2\ in\ water\ (after\ desorption)$$

Based on graph average mole fraction of CO_2 in water successfully desorbed against temperature in figure 4-2 next page, it clearly convey the initial claim that amount of CO_2 desorbed is higher at high temperature. From the graph, it can be see that mole fraction of CO_2 in water which are desorbed increase as temperature increase. At temperature 313K, average mole fraction of CO_2 in water that are desorbed is 0.000318 and increase up to mole fraction 0.000597 at temperature 353K. This indicates that more CO_2 release during desorption at high temperature compare to low temperature. However

the trend of increasing is not linear. From the graph, it can be said that at temperature 313K to 333K, the gradient of the graph is much steeper compare to at high temperature tested (343K to 353K). This mean that the change in amount of CO_2 desorbed is higher at temperature 313K to 333K compare to the change at temperature 343K to 353K.

As temperature increase, desorption of dissolve CO_2 in water also increase. This is due to the increase in nucleation rate. Basically nucleation rate is reflect by the bubble formation. As stated early, more bubble formation result in more desorption of CO_2 from water. Results for this part shows the agreement with classical nucleation theory (CNT). Equation for the CNT as proposed by Lubetkin (1995) is as follow where N_{nucl} is the nucleation rate, C_o is the initial concentration and T refer to temperature of the fluid.

$$N_{nucl} = C_o \exp\left(\frac{-\Delta G_{nucl}}{KT}\right) \qquad (Lubetkin, 1995)$$

According to prediction by CNT, nucleation rate effect by several factors including temperature. At constant pressure and concentration, nucleation rate will be increase as temperature increase (Santra, Chakrabarty & Baghchi, 2008). Increase in nucleation rate mean that more bubbles will form and escape from the fluid (Oxtoby, 1995). Thus, it can be say that result of this experiment proved the prediction of CNT in which increase in temperature will lead to increase in desorption of CO_2 given initial CO_2 and pressure are constant.

Besides through concept of CNT, results from this experiment also can be explain through supersaturated ratio concept. Table 4-2 next page shows supersaturated ratio calculated at each temperature tested. According to Shiba and Okawa (2005), supersaturated ratio can be calculated by dividing initial mole fraction of CO_2 in water with mole fraction at equilibrium condition 1 bar as follow:

$$Supersaturated\ ratio, S = \frac{initial\ mole\ fraction}{mole\ fraction\ at\ equilibrium\ 1\ bar}$$

Referring to table 4-2 below, it is noticed that as temperature increase, supersaturated ratio also be increase. Theoretically, supersaturated ratio can reflects the tendency of dissolved gas to release from solvent. Higher supersaturated ratio, higher tendency of gas to release (Shiba, 2005).This statement support the result of the experiment in which in this experiment, as temperature increase, supersaturated ratio also increase significantly. As supersaturated ratio increase, CO_2 will be more favourable to release from water. As a result of that, more CO_2 desorbed from water at high temperature compare to low temperature.

TABLE 4-2 : Supersaturated Ratio at Respective Temperature

Temperature (K)	**Initial Mole Fraction** $(\frac{mol\ CO_2}{mol\ H_2O})$	**Mole fraction at VLE 1 bar** $(\frac{mol\ CO_2}{mol\ H_2O})$	**Supersaturated Ratio,S**
313	0.001	0.00043	2.33
323	0.001	0.00036	2.79
333	0.001	0.00030	3.29
343	0.001	0.00026	3.85
353	0.001	0.00024	4.26

#mole fraction of CO_2 in water at VLE 1 bar is calculated using Henry's Law and RK EOS

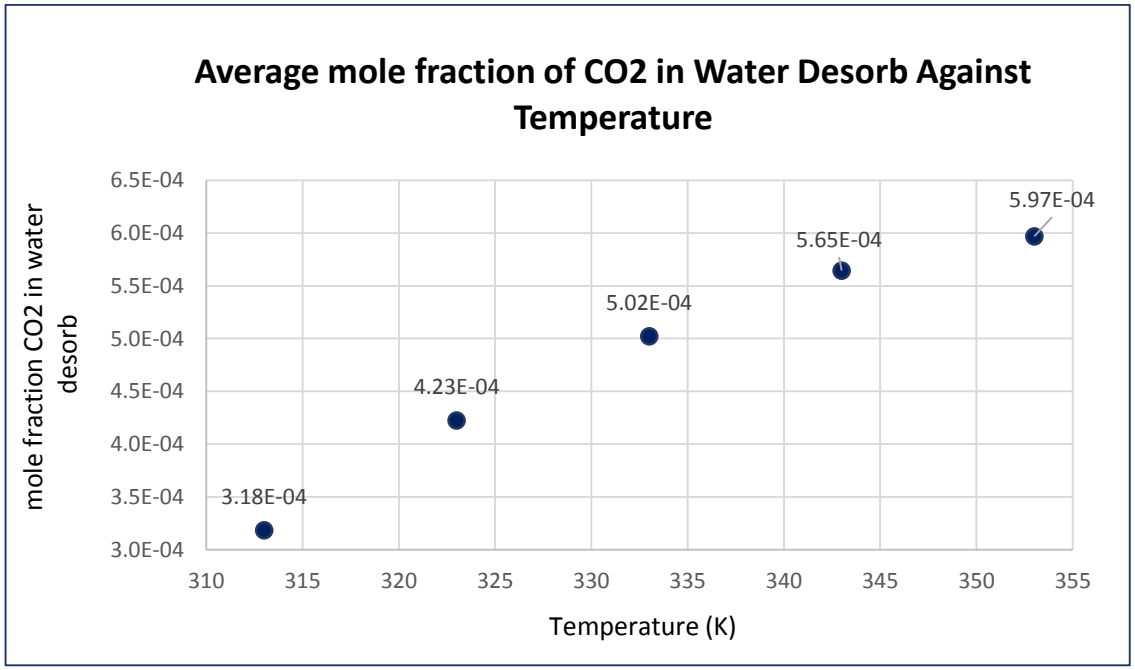

FIGURE 4-2 : Graph of mole fraction of CO_2in water desorb against temperature

4.1.2 Effectiveness of Desorption at Different Temperature

Besides investigate effect of temperature towards desorption, measure the effectiveness of desorption of dissolved CO_2 from water at different temperature by using converging nozzle also is one of the objectives of this research. To prove the effect of temperature towards desorption using converging nozzle (subsection 4.1.1) better and to measure the effectiveness of desorption at different temperature, the mole fraction of CO_2 in water after desorption process take place are compared with mole fraction at vapour liquid equilibrium (VLE) condition at 1 bar (atmospheric pressure) as shown in graph in figure 4-3. Referring to the graph in figure 4-3 next page, as temperature increase, mole fraction of dissolved CO_2 after desorption will be decrease. Same goes to the mole fraction of CO_2 at equilibrium 1 bar. However, it can be noticed that in the graph in figure 4-3, as temperature increase, the mole fraction of CO_2 in water after desorption tends to converge towards VLE line plotted. This is proved clearly through graph of deviation from VLE against temperature as shown in figure 4-4. Deviation from VLE at respective temperature calculated as follow:

$$Deviation\ from\ VLE = mole\ fraction\ of\ CO_2\ in\ water\ after\ desorption - mole\ fraction\ of\ CO_2\ in\ water\ at\ VLE\ (1bar)$$

From graph in figure 4-4, it clearly show that as temperature increase, the deviation of mole fraction of dissolved CO_2 from the VLE decrease that is from 0.00025 at temperature 313K down to 0.00017 as temperature increase to 353K. This convey the initial analysed clearly which is as temperature increase, mole fraction of CO_2 in water after desorption decrease and tends to converge towards mole fraction of dissolved CO_2 at VLE condition (1 bar).

Basically, VLE line can be refer as maximum mole fraction of CO_2 in water in which it can decrease to. VLE can be considered as ideal case as the system already achieved equilibrium condition. In this research, mole fraction of CO_2 dissolved in water at 1 bar are calculated using Henry's Law by taking into consideration the fugacity and activity coefficient of CO_2 . The modified Henry's Law used to calculate can be refer at page 18 Chapter 2. The fugacity coefficient at different temperature were determined using Redlich-Kwong (RK) EOS as suggested by Gainar et al.(2005).

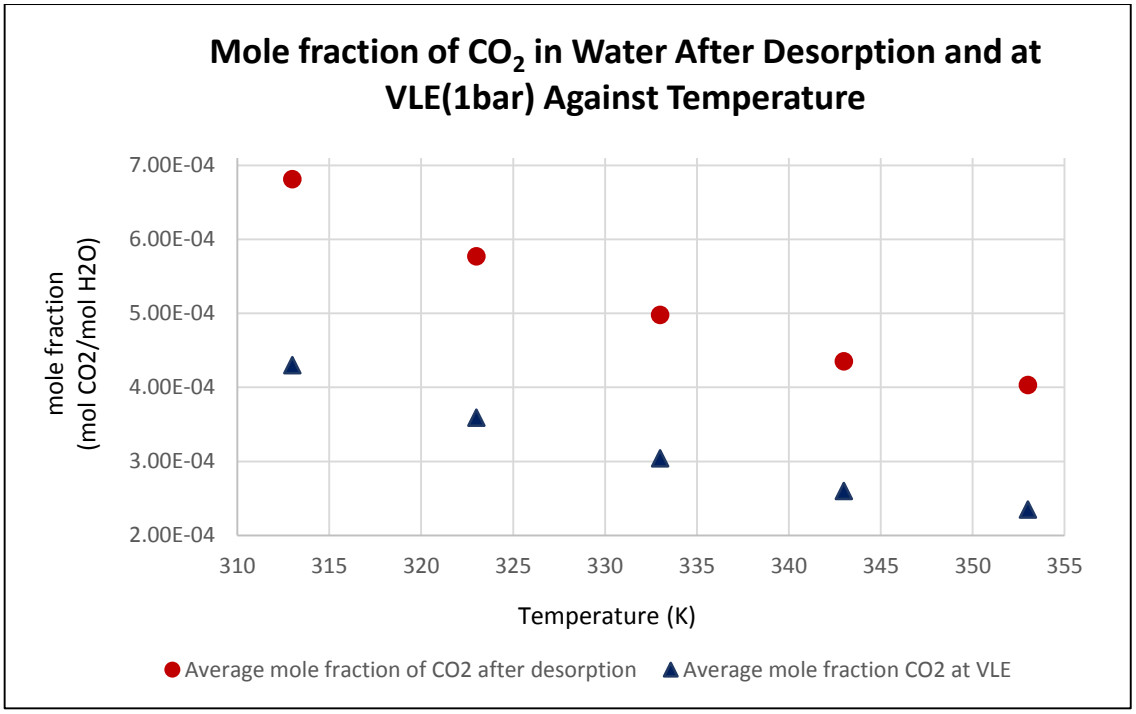

FIGURE 4-3 : Comparison Graph of mole fraction of CO_2in water After Desorption with Equilibrium at 1 bar.

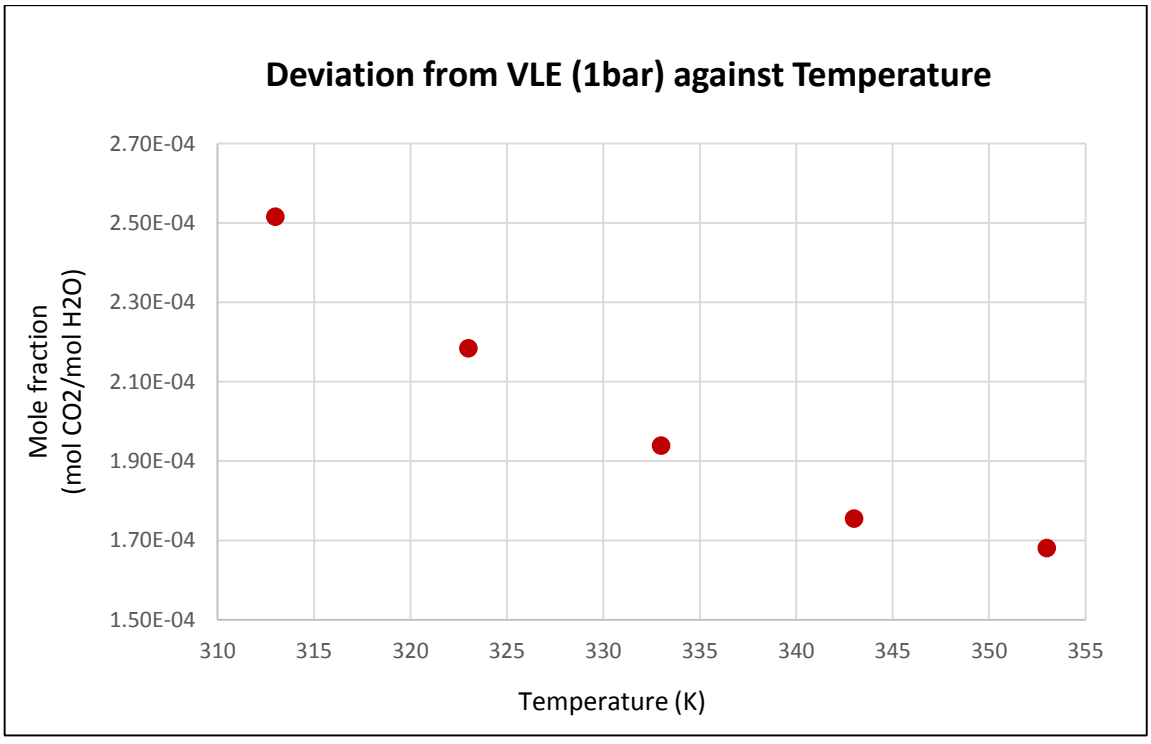

FIGURE 4-4 : Graph Deviation of mole fraction of CO_2 in water after desorption with the VLE (1 bar) against temperature

From mole fraction of CO_2 in water after desorption and at equilibrium 1 bar, effectiveness of the desorption using converging nozzle at different temperature of water can be determined. The efficiency of desorption at respective temperature was calculated as follow where initial mole fraction is constant at 0.001 mol CO_2/ mol H_2O :

$$Efficiency\ (\%) = \frac{initial\ \ mole\ fraction\ CO_2 - mole\ fraction\ CO_2\ after\ desorption}{initial\ mole\ fraction\ CO_2 - mole\ fraction\ CO_2\ at\ VLE} \times 100\ \%$$

Graph in figure 4-5 page 39 shows percentage of efficiency of desorption process at different temperature. The graph is plot based on average amount of CO_2 desorbed at different temperature during experiment with the maximum amount of CO_2 that can be desorbed until reach equilibrium state at 1 bar using formula above. Data used for the determination of efficiency is presented in table 4-3 next page. Referring to the graph efficiency against temperature in figure 4-5 , it clearly show that as temperature increase, the efficiency of converging nozzle to desorbed dissolved CO_2 in water also increase and can reach up to 78.03% at 353K. However, the trend of increasing efficiency is not linear. At temperature 313K, the efficiency of desorption are 55.87% and this percentage increase to 72.15% at temperature 333K. From temperature 333K and above, the increase of the efficiency start to be small and almost the same for temperature 343K and 353K.

Beside through CNT explained early in the discussion, this phenomenon also can be described by concept of solubility of CO_2 in water system. As the temperature increase, solubility of CO_2 in water will be decrease (El Hajj,Al-Hindi and Azizi, 2005; Shapley, 2013). Due to that, CO_2 tends to desorb more from water at high temperature compare to at low temperature. This concept of solubility of CO_2 in water system also explain the trend of increasing of the effectiveness of desorption in which change in effectiveness is higher at temperature 313K to 333K compare to change of effectiveness at 343K to 353K (gradient of the graph is steeper from temperature 313K to 333K compare to from 343K to 353K).

As temperature increase to more than 343K, change in decrease of solubility become less significance (Diamond & Akinfiev, 2003). Refer figure 2-9 page 17 for the

solubility graph of CO_2 in water by Shapley (2013). As there is only small decrease in solubility at high temperature, the increase of efficiency of desorption also less significance at high temperature compare to at lower temperature tested.

Result for this part show the agreement with report made by El-Hajj et al.(2014), Tobiesen (2008), and Kelogg (1965). All of these authors claimed that for desorption of CO_2 from water system, mass transfer increase as temperature increase. Relate it with this research, increasing in mass transfer reflect in increasing of amount of CO_2 release. Result of it leads to more CO_2 desorbed from water at high temperature given that the initial concentration of CO_2 is constant. Hikita and Nikisha (1985) through their experiment using agitated vessel also reported high mass transfer at high temperature.

TABLE 4-3 : Data Use for Efficiency Determination

Temperature (K)	**Average mole fraction desorbed (initial – final)** $(\frac{mol\ CO_2}{mol\ H_2O})$	**Mole fraction CO_2 can be desorbed until reach VLE (1bar)** $(\frac{mol\ CO_2}{mol\ H_2O})$	**Efficiency (%)**
313	0.00032	0.00057	55.87
323	0.00042	0.00064	65.93
333	0.00050	0.00070	72.15
343	0.00056	0.00074	76.29
353	0.00060	0.00077	78.03

 # mole fraction CO_2 that can be desorbed until reach VLE calculated by subtracting 0.001 mole fraction (initial) with mole fraction of dissolved CO_2 at VLE (1bar) at respective temperature.

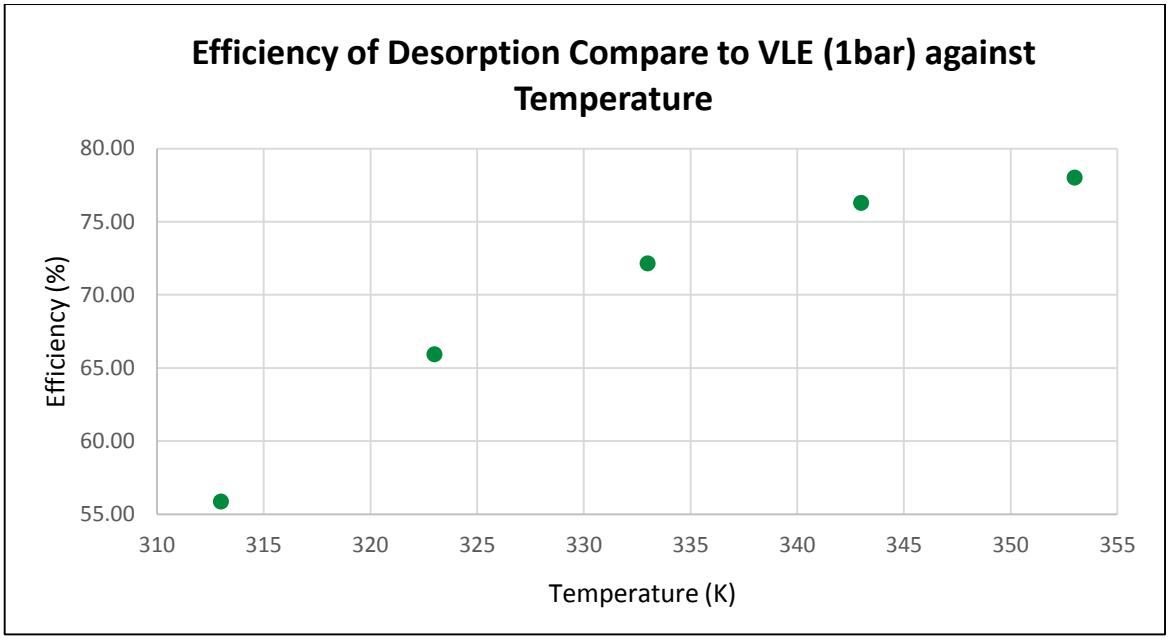

FIGURE 4-5 : Graph of efficiency of desorption when compare to VLE at 1 bar against temperature.

Next chapter will describe precise conclusion for this research project and also some recommendations to improve it and for the future works.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Most of world's reserve natural gas contain high amount of CO_2 and need to be treated. Common ways to remove CO_2 is through absorption and desorption technique. Converging nozzle change the conventional desorption column with more feasible and convenient compact size separator that can be used at offshore platform.

In conclusion, this research project clearly shows the effect of temperature towards desorption of dissolved CO_2 from water by using converging nozzle. The effectiveness of desorption of CO_2 at different temperature also be convey.

Through the data recorded from laboratory work and also analysing and discussion made based on the collected data, it can be conclude that as temperature increase, amount of CO_2 release from water also increase, given other parameters are kept constant. At higher temperature, there will be more dissolved CO_2 desorbed from water compare to at low temperature.

The trend of increasing of desorption of CO_2 with water highly depending on the trend of solubility of CO_2 itself in the water system. Same goes to the effectiveness of desorption of CO_2. This research showed that effectiveness of the physical desorption of dissolved CO_2 from water by using converging nozzle increase as temperature increase. The effectiveness can go up to 72% at temperature 353K. However, at high temperature the increase in effectiveness become less significance.

In a short, all the objectives of this research successfully achieved. The effect of temperature towards desorption of CO_2 as well as the effect towards effectiveness of desorption using converging nozzle clearly conveyed.

5.2 Recommendations and Future Work

Recommendation to improve this project can be categorized in two scopes which are on the improvement of the methods or equipment itself and much more important the future works to expand the research.

For the improvement of the method or equipment, recommendations are as follow:

i. the insulator should be install at every point where temperature need to be maintain. This is because varying the temperature is the key in this project. Any heat lost to the surrounding will result in the drop of temperature from the studied temperature.
ii. CO_2gas analyser should be install so that amount of CO_2 can be determine more accurately.

Recommendations for the future works are listed as below:

i. Increase the range of temperature of the test of desorption. The research can be done at the very high temperature and also very low temperature of solvent.
ii. Test on desorption of CO_2 be done by varying other parameters such as at high and low pressure as well as at high and low CO_2 loading. This research conducted at constant pressure and low concentration of CO_2. In order to determine properties of physical desorption and also the optimum condition and limitation of the converging nozzle, research can be expand by varying other parameters such as pressure.
iii. Study be done by using other solvent (absorbent). Water use in this research is just as a medium to show how CO_2 desorbed from the solvent. Further study can be done by using other type of solvent that usually use in the pre-treatment section of natural gas such as amine-based solvent.

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APPENDICES

Appendix A : An internal view of the packed column

Appendix B : Process Flowsheeting For Matrix Modified

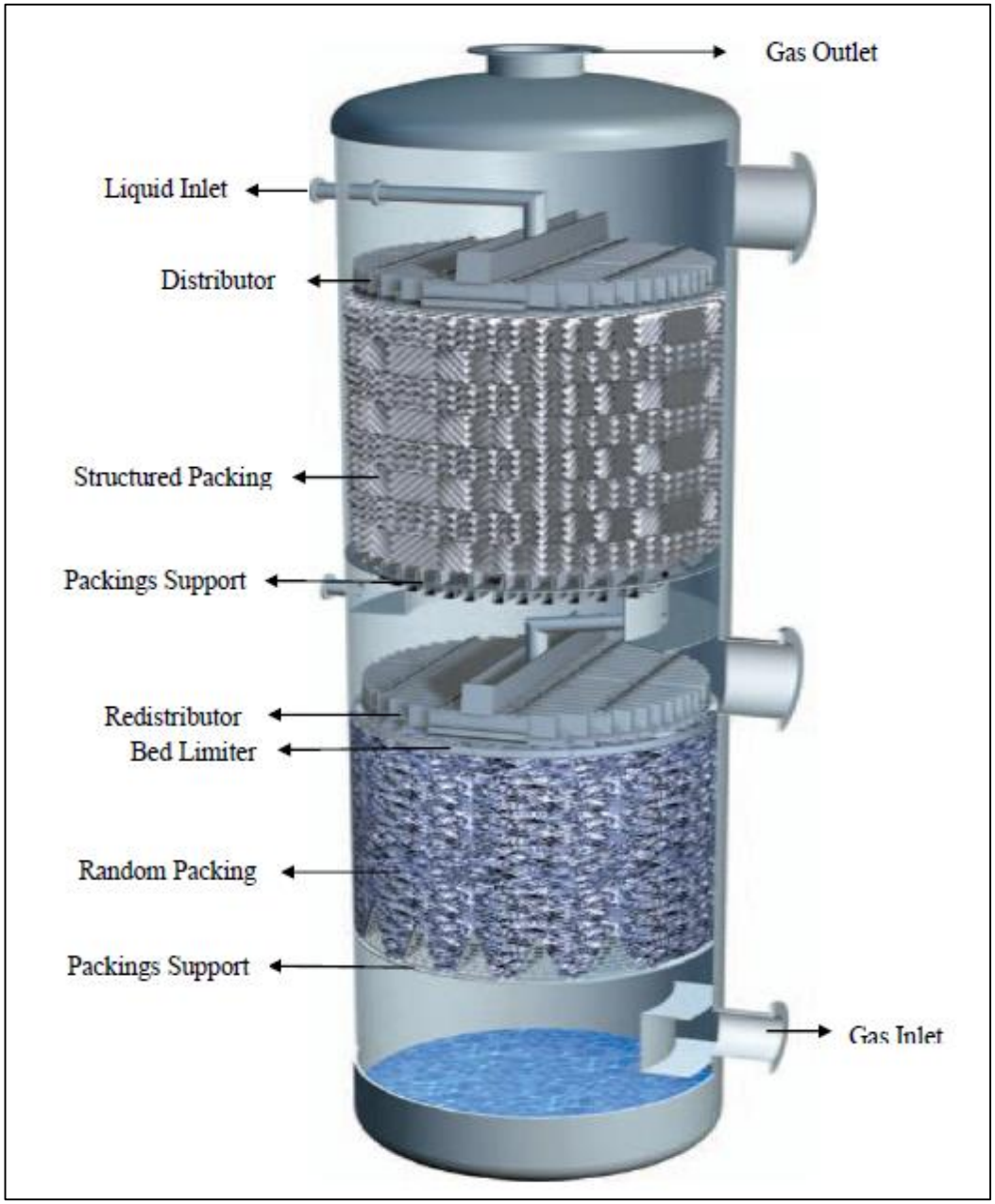
Appendix C : Data for Solubility of CO_2in water

Appendix D : Process Flow Diagram of the Equipment Use for the Project

Appendix E : Picture of the Test Rig (equipment used)

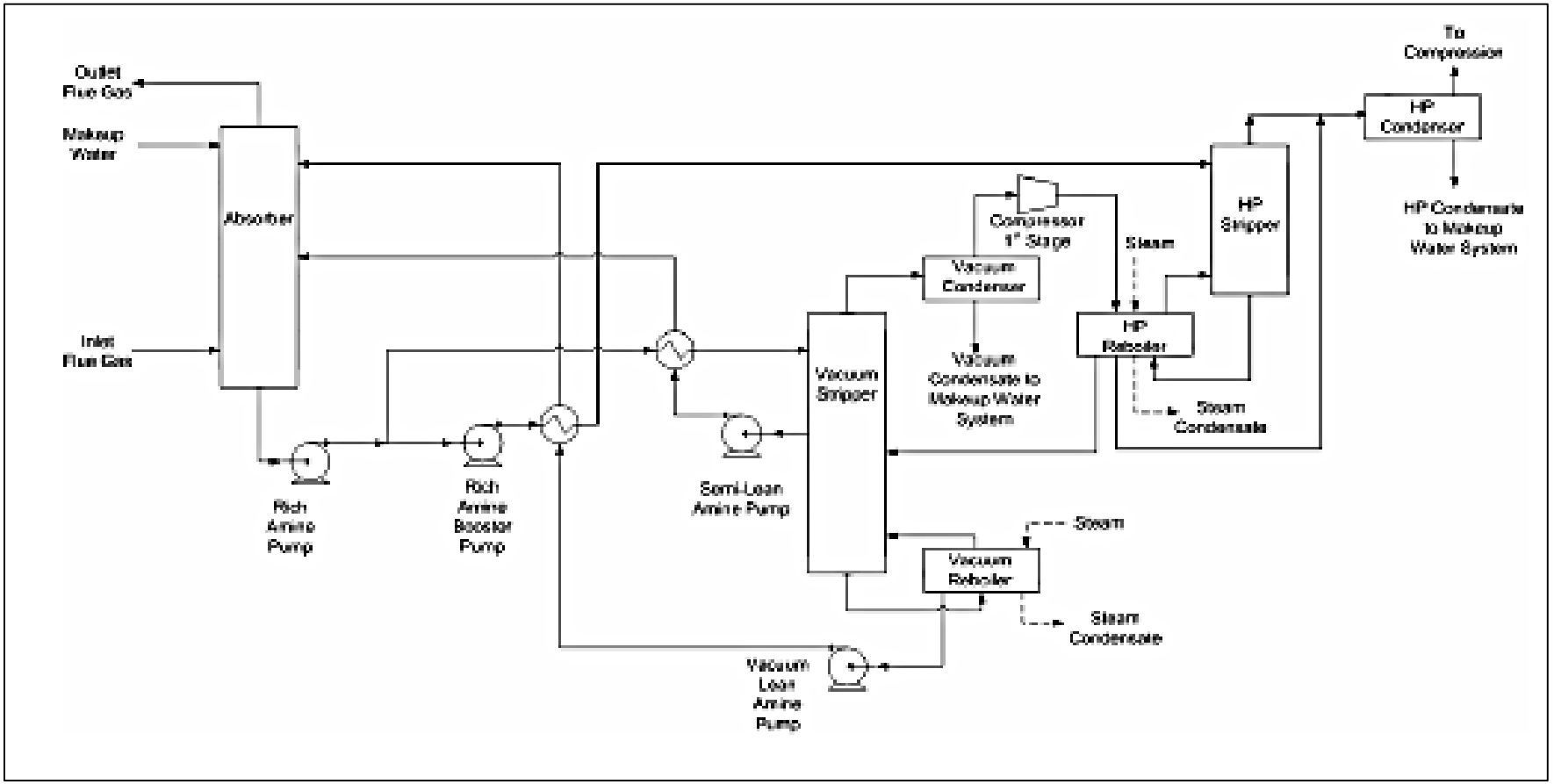
Appendix F : Results for Amount of CO_2 in term of Volume

APPENDIX A: An internal view of the packed column



Appendix A: An internal view of the packed column *(Source: Sulzer, 2010*

APPENDIX B : Process Flowsheeting For Matrix Modified



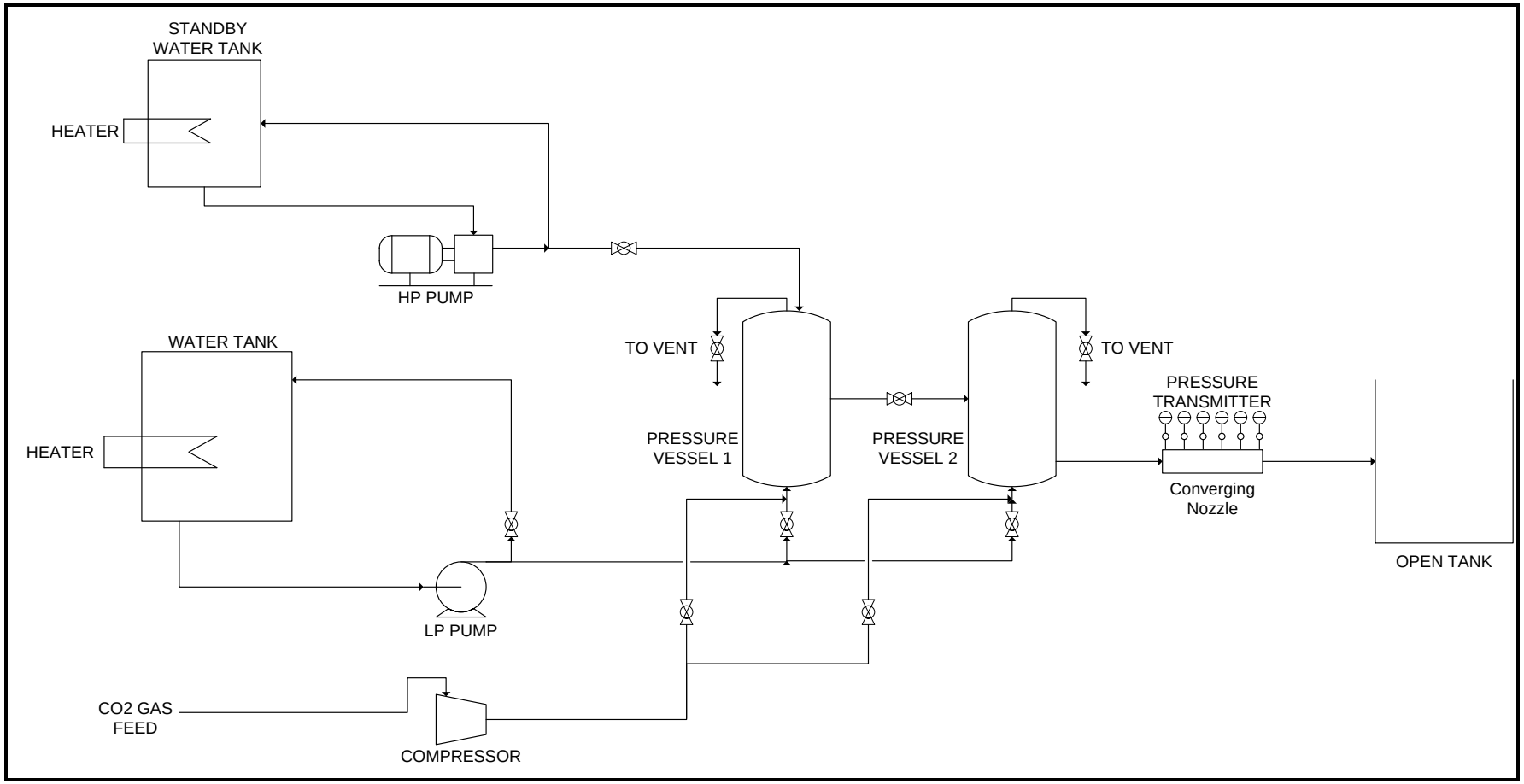
Appendix B – Process Flowsheeting For Matrix Modified Stripper proposed by Oyenekan and Rochelle (2007)
(source of diagram : Advance CO2 Capture Technology, International Journal of Greenhouse Gas control (2008))

APPENDIX C : Data for Solubility of CO_2 in water

	1000 x mole fraction of CO_2 in liquid phase						
	Partial pressure of CO_2 in kPa						
t/°C	5	10	20	30	40	50	100
0	0.067	0.135	0.269	0.404	0.538	0.671	1.337
5	0.056	0.113	0.226	0.338	0.451	0.564	1.123
10	0.048	0.096	0.191	0.287	0.382	0.477	0.950
15	0.041	0.082	0.164	0.246	0.327	0.409	0.814
20	0.035	0.071	0.141	0.212	0.283	0.353	0.704
25	0.031	0.062	0.123	0.185	0.247	0.308	0.614
30	0.027	0.054	0.109	0.163	0.218	0.271	0.541
35	0.024	0.048	0.097	0.145	0.193	0.242	0.481
40	0.022	0.043	0.087	0.130	0.173	0.216	0.431
45	0.020	0.039	0.078	0.117	0.156	0.196	0.389
50	0.018	0.036	0.071	0.107	0.142	0.178	0.354
55	0.016	0.033	0.065	0.098	0.131	0.163	0.325
60	0.015	0.030	0.060	0.090	0.121	0.150	0.300
65	0.014	0.028	0.056	0.084	0.112	0.140	0.279
70	0.013	0.026	0.052	0.079	0.105	0.131	0.261
75	0.012	0.025	0.049	0.074	0.099	0.123	0.245
80	0.012	0.023	0.047	0.070	0.093	0.116	0.232
85	0.011	0.022	0.044	0.067	0.089	0.111	0.221
90	0.011	0.021	0.042	0.064	0.085	0.106	0.211
95	0.010	0.020	0.041	0.061	0.082	0.102	0.203
100	0.010	0.020	0.039	0.059	0.079	0.098	0.196

Appendix C : Solubility of CO_2 in water data over a wide range of temperature and pressure. The estimated uncertainty is about 2%. *(source : Smith,2005)*

APPENDIX D : Process Flow Diagram of the Equipment Use for the Project



APPENDIX D : Process Flow Diagram of the Equipment Use for the Project

APPENDIX E : Picture of the Test Rig (equipment used)

Equipment Used (two pressure vessels covered with insulator are for absorption while the uncovered for desorption)

Temperature controller to control water temperature and pressure drop indicator

Pressure Indicator

APPENDIX E : Picture of the Test Rig (equipment used)

InletCO_2 gas control and compressor

Water tank equipped with heater besides temperature controller

Device used to collect the water sample (with pipe inner volume 20mL and pressure chamber)

Location of sampling point and pressure transmitter

Appendix F: Results for Amount of CO_2 in term of Volume

TABLE F-1 : Amount of CO_2 after desorption in term of volume (before convert into mole fraction)

Temperature (K)	**Pressure (bar)**	**Final amount of CO_2 (after desorption)** *(mL CO_2/20mL water sample)*			
		1st run	***2nd run***	***3rd run***	***Average***
313	15	18.8	18.5	18.9	18.7
323	15	16.7	16.4	16.8	16.6
333	15	15.2	14.9	15.3	15.1
343	15	14.1	13.8	14.2	14.0
353	15	13.3	13.0	13.4	13.2

#uncertainty for measuring cylinder used is ± 0.1 mL